A method for quantitative characterization of agglomeration degree in nanocomposites

Characterization of filler dispersion state using the effective dielectric constant: a theoretical study

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Abstract

Achieving a quantitative tool for the characterization of dispersion in composites is a challenge. Effective dielectric constant of composites varies with changes in inter-particle interactions which originate from changes in inter-particle spacing. In this respect, a novel methodology has been introduced to relate the dispersion state of composites to their effective dielectric constant. Total filler volume fraction, volume fraction of particles inside agglomerates and size of agglomerates are considered as dispersion factors which affect the effective dielectric constant. Inter-particle interactions are calculated based on the introduced dispersion factors. It is shown that the effective dielectric constant of composites increases with filler concentration and agglomeration due to increased inter-particle interactions. Growth of agglomerates size and volume fraction of particles inside the agglomerates result in further enhancement of effective dielectric constant. This increment is abrupt at percolation where the particles or agglomerates approach each other and the inter-particle interactions are pronounced. It is possible to characterize the dispersion state of a composite with given effective dielectric constant and filler volume fraction using the developed effective dielectric constant.

Keywords: effective dielectric constant; dispersion state; agglomerate packing density; agglomerate size

1. Introduction

The properties of composites depend not only on the properties of the individual constituents but also on the extent of filler dispersion. In most cases dispersion is not ideal and agglomeration of particles is anticipated especially at higher volume fractions [1-3]. Agglomerates with different sizes and particle packing densities are formed in nanocomposites which affect the final macroscopic properties. Hence, it is a challenge to identify the degree of dispersion and to correlate a relationship between microstructure and final macroscopic properties [4, 5].

Various visual techniques such as XRD, TEM and AFM have been utilized to identify the dispersion degree. However, they are restricted to a small area of the specimen which does not necessarily represent the whole sample. Additionally, it is often difficult to interpret their results and to reach useful quantitative data [6]. Measurement of macroscopic properties such as mechanical, rheological, electrical and dielectric properties has also been used for evaluating the microstructure. However, they cannot generate a quantitative prediction of filler dispersion state. Often these methods have been used in combination with image microscopy, but still they have their limitations. Hence, there is a necessity to modify and upgrade quantitative characterization techniques for dispersion [7-9].

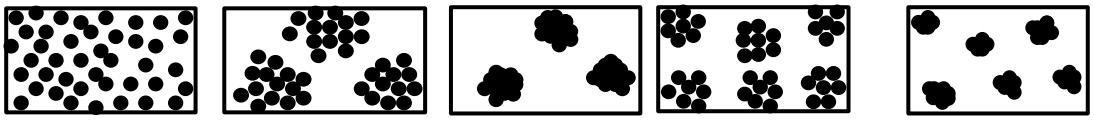
There has been a tremendous amount of research on the relationship between microstructure and dielectric properties of composites and nanocomposites [10, 11]. One of the major advantages of dielectric analysis is that it can be applied as a non-destructive testing method

for dispersion analysis [12]. In addition, it is possible to detect filler-filler interactions directly as dipole-dipole interactions between polarized particles [13, 14]. In composites comprised of dielectric particles inside a non-polar polymers (with low dielectric constant), the effective dielectric constant at relatively high frequencies is only affected by the concentration and dispersion state of dipoles [15-17]. This means that, at the same filler content, changes in filler dispersion has an impact on the amount of inter-particle interactions and consequently the value of the effective dielectric constant. In fact, several studies have shown that agglomeration of dielectric particles in a non-dielectric polymer results in enhancement of effective dielectric constant due to increased inter-particle interactions [18, 19].

Based on the above statements, it seems possible to track filler dispersion state by relating the changes in inter-particle interaction in respect to filler dispersion state to the effective dielectric constant. The local field method can be applied to relate the microstructure to the effective dielectric constant. However, the term associated with inter-particle interactions is often neglected from the calculations of the local field by assuming regular (symmetrical) arrangement of particles [20-22]. So, the resultant effective dielectric constant is usually an underestimate of its experimental value especially at higher filler volume fractions or in case of filler agglomeration where the magnitude of inter-particle interactions is noticeable [23]. Although there have been some attempts for including the effect of inter-particle interactions [24-26], none have developed a useful relation between filler dispersion state and the effective dielectric constant of composites.

Hence, it seems possible that the impact of inter-particle interactions on the effective dielectric constant can be acknowledged by calculating the local field with respect to filler

dispersion state. Here we have used this approach to foresee the impact of filler dispersion state on the effective dielectric constant of composites for the first time and to use this relation as a novel tool for characterization of filler dispersion state. Various possible dispersion states can be considered based on; total volume fraction of particles, volume fraction of particles inside the agglomerates (agglomerate packing density) and agglomerate size. This is demonstrated in Fig. 1. To relate composite microstructure to the effective dielectric constant, inter-particle interactions are calculated in respect to various possible dispersion states based on the discussed factors.



a **b** **c** **d** **e**

In an extension to this research, an experimental design is established in order to create different dispersion states based on the introduced dispersion factors and dielectric analysis is performed to measure their effective dielectric constant. The achieved results are interpreted and tested against the developed model. Due to the printing limitations, the results of this part will be presented in the future as the second part of this research.

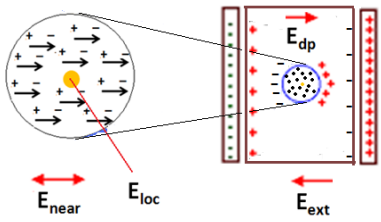
2. Relationship between filler dispersion and effective dielectric constant

The effective dielectric constant is related to the local electric field ($\mathbf{E}_{loc}$) through macroscopic polarization [21]. The local field acting on a dipole is influenced by the surrounding medium and therefore can deviate from the external field. The local field is in fact due to the external field as well as all other dipoles in the system [22]. As demonstrated by Lorentz, the dipole at which the local field acts on is imagined to be surrounded by a

spherical cavity whose radius is sufficiently large that the outside medium can be treated as a continuous medium. The interaction of the probe dipole with other dipoles inside the cavity is however treated microscopically [20]. Therefore, the arrangement of neighboring dipoles in respect to the probe dipole should to be taken into account. This is where the effect of dispersion can be reflected in the value of the local field and ultimately the effective dielectric constant. The local field, acting on the central dipole, is thus given by the sum [22]:

$$\mathbf{E}_{loc} = \mathbf{E}_{ext} + \mathbf{E}_{dp} + \mathbf{E}_{s} + \mathbf{E}_{near} \quad (1)$$

As demonstrated in Fig. 2, $\mathbf{E}_{ext}$ is the external field, $\mathbf{E}_1$ is the depolarization field, i.e. the field due to the polarization of charges lying at the external surfaces of the sample, $\mathbf{E}_s$ is the field due to the polarization of charges lying on the surface of the Lorentz sphere. $\mathbf{E}_{near}$ is the field due to other dipoles lying within the sphere and it is known as the near field [21, 22].



As shown in the literature, $E_{ext}+E_{dp}=P/3\varepsilon_m$ where P is the macroscopic polarization and ε_m is the dielectric constant of the matrix [20]. The magnitude and direction of the near field ($\mathbf{E}_{near}$) depends on the arrangement of dipoles within the cavity and it is the sum of the electric field at the center of the cavity due to nearby dipoles ($\mathbf{p_i}$) at various distances ($\mathbf{r_i}$) from the origin. So; $E_{near} = \sum_1^n \mathrm{E}(\mathrm{p_i}, \mathrm{r_i})$. $\mathrm{E}(\mathrm{p_i},\mathrm{r_i})$ is expressed by:

$$\mathrm{E}(\mathrm{p},\mathrm{r}) = [3(\mathrm{p}.\mathrm{n_r})\mathrm{n_r} - \mathrm{p}]/4\pi\varepsilon_m\mathrm{r}^3 \quad (2)$$

Where, n_r is the unit vector of r and $\boldsymbol{\varepsilon_m}$ is the dielectric constant of the matrix [21].

The dipole moments of all particles are assumed to be in the same direction and have equal magnitude when an electric field is applied; i.e. $\mathbf{p_i=p_j=p}$. We only consider the contributing fields in the direction of the external field (e.g. the x vector). Since the formed dipoles oppose the applied external field, E(p,r) can be written as:

$$E(p, r_i) = -p\,(3\cos^2\theta_i \sin^2\phi_i - 1)/(4\pi\varepsilon_m\, r_i^3) \quad (3)$$

$E(p,r_i)$ given by the above equation is in fact the scalar component of vector $E(p,r_i)$ in the direction of the applied field. θ is the angle between the x vector and the projection of r vector onto the xy plane. ϕ is the angle between r and the z vector. $\boldsymbol{\theta}$ ranges from 0º to 360º, ϕ is in the range of 0º to 180º and **r** is the distance from the origin to the center of a surrounding particle (the inter-particle distance).

$\sum_1^n E(p, r_i)$ represents the contribution from all dipoles within the cavity. For evaluating the contribution of $\sum_1^n E(p, r_i)$ to the local field, one has to sum over the fields of individual dipoles. We know that the dipole moment (p) of a spherical particle is linearly related to the local field through its polarizability ($p=\alpha E_{loc}$) [20, 21]. From the definition of polarizability for a spherical particle in a medium with dielectric constant ε_m, we have:

$$\sum_1^n E(p, r_i) = -\frac{(\varepsilon_f - \varepsilon_m)}{(\varepsilon_f + 2\varepsilon_m)} R^3 E_{loc} \times \sum_1^n \frac{3\cos^2\theta_i \sin^2\phi_i - 1}{(r_i^3)} \quad (4)$$

By looking at Eq. 4, it is possible to define a geometrical factor which we refer to as the 'A parameter' with the magnitude of $-\sum_1^n (3\cos^2\theta_i \sin^2\phi_i - 1)\, R^3/r_i^3$. Parameter A is dependent on the location of the particles inside the cavity in relation to the probe particle;

i.e. the orientation of surrounding particles and their inter-particle distances in respect to the probe particle. In other words, the A parameter is a function of microstructure which can influence the magnitude of the local field. Based on Eq. 4, it can be shown that when the particles are located in a cubic lattice with the same inter-particle distance from the probe particle, A=0 and E_{near} vanishes. However, when the particles are not arranged symmetrically, parameter A is not necessarily zero.

To calculate $\sum_1^n E(p, r_i)$, first and foremost the size of the imaginary cavity should be set in order to have an estimation of the number of particles inside the cavity which contribute to the near field. The size of the cavity should be much larger than the distance between the particles [20-22]. The average inter-particle distance can be considered as a scale for the radius of the imaginary cavity. For uniform distribution of particles, the probe particle is surrounded by 6 contiguous particles with inter-particle distance; $d_{ave} = R\,(4\pi/3\emptyset_f)^{\frac{1}{3}}$. Where $\emptyset_f$ is the particles volume fraction and R is the particle radius [27]. Hence, the radius of the cavity (R_c) should be large enough to hold in all 6 particles; $R_c=d_{ave}+R$.

For a disordered (or random) distribution, the number of particles inside the cavity besides the probe particle ($\mathbf{n_c}$) can be estimated mathematically as a function of filler volume fraction ($\emptyset_f$) and particle radius (R):

$$n_c = (0.52)\emptyset_f(R_c/R)^3 - 1 \qquad (5)$$

Thus, the probe particle at the center of the presumed cavity is surrounded by n_c number of particles distributed randomly within the cavity. Coefficient 0.52 is deduced from dividing the volume of a sphere with radius R_c by the volume of a cube with length 2Rc.

In a random distribution, particles in the neighborhood of the probe particle can be located anywhere from r=2R to r=d_{ave} inside the cavity. To consider randomness in particle distribution, a rather simple program was written in MATLAB software to obtain the amount of A parameter as a function of filler volume fraction (Appendix A). It should be pointed out that for random distribution of particles, parameter A is a function of d_{ave}/R which is related to particle volume fraction and not directly dependent on particle size. To consider the randomness in distribution of particles, the A parameter is calculated repeatedly (1000 runs) and the average value is considered as the final value. For every filler volume fraction a unique value is obtained for the A parameter. The obtained A parameters as a function of filler volume fraction are presented in table 1.

$\emptyset_f$	d_{ave}/R	n_c	R_c/R	A
0	0	0	0	0
0.1	3.5	3.6	4.5	0.07
0.2	2.8	4.5	3.8	0.13
0.3	2.4	5.2	3.4	0.18
0.4	2.2	5.7	3.3	0.23
0.5	2	6.2	3	0.29

From Table 1, it can be seen that the value of A parameter increases with increase in particle volume fraction with an almost linear trend. Therefore, the A parameter can be written as a function of filler volume fraction; $A \approx 0.6\emptyset_f$. Thus, the near filed is:

$$E_{near} = AE_{loc}\,(\varepsilon_f - \varepsilon_m)/(\varepsilon_f + 2\varepsilon_m) \quad (6)$$

The local field for a random distribution of particles is achieved by taking into account the value of the near field calculated above. Now from the relation between dielectric

displacement, effective dielectric constant, polarization and the local field [21], the effective permittivity can be obtained through the achieved modified version of the local field:

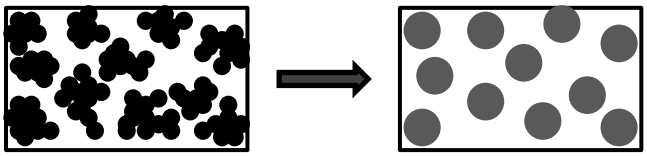
$$\varepsilon_{eff} = \varepsilon_m + 3\varepsilon_m \varnothing_f(\varepsilon_f - \varepsilon_m)/[\varepsilon_f + 2\varepsilon_m - (\varnothing_f + A)(\varepsilon_f - \varepsilon_m)] \quad (7)$$

Eq. 7 generates the effective permittivity of a composite with random distribution of mono-dispersed particles at various filler volume fractions by taking into account the effect of interactions between nearby particles. It can be seen that the Maxwell-Garnet formula [26] is retrieved when the A parameter is dropped. It is worth mentioning that based on equation 7, if we place $\varepsilon_{eff}=\varepsilon_f$, then $Ø_f$ equals to 0.65 when $\varepsilon_m=1$ and $\varepsilon_f=10$. This is in fact very close to the maximum volume fraction for random packing of same sized particles.

The obtained A parameter above is for the case of random dispersion of particles which is quite ideal in composite materials. Now, we need to take the effect of various dispersion states and agglomeration into account. Dispersion degree is related to the distance between particles and it reduces as the particles assemble into agglomerates. In other words, dispersion degree can be viewed as a function of particle packing density inside agglomerates (or the distance between neighbouring particles inside agglomerates) and the relative distance of agglomerates themselves. Accordingly, the inter-particle interactions differ based on the dispersion state resulting in different effective dielectric constants. The different dispersion scenarios presented in Fig. 1 can be used as reference for calculating the A parameter.

In an agglomerated microstructure, the particles are assumed to be dispersed randomly within the agglomerates. In a way, the agglomerate can be thought of as a composite with random dispersion of particles with relatively high volume fraction. The formed agglomerates are

assumed to be spherical and identical in terms of size and number of primary particles, and they are randomly distributed inside the matrix. This is demonstrated in Fig. 3. A microstructure can vary based on volume fraction of particles inside the agglomerates and agglomerate size.



To calculate the effective dielectric constant as a function of particle dispersion state, once again we need to establish the Lorentz cavity. Then the value of the near field as a measure of inter-particle interactions is calculated. The Lorentz cavity should be large enough to include an agglomerate. The particles located at the inner core of the agglomerates (n_{fa}) in respect to the particles on the outer surface of the agglomerate (n_{fs}) are surrounded by roughly double the number of particles. Hence, the magnitude of inter-particle interactions for the inner particles is expectedly double the magnitude of inter-particle interactions for the boarder particles. Since the agglomerates resemble a composite with relatively high filler volume fraction, the near filed can be calculated with the same approach discussed for the case of random dispersion of particles. So, for the inner particles, the A value is expected to be linearly dependent on the volume fraction of particles inside the agglomerate ($0.6ø_{fa}$). For the particles on the outer surface of the agglomerate the A value is expected to be half the predicted value for the inner particles ($0.3ø_{fa}$). So, the total A parameter is comprised of two parts:

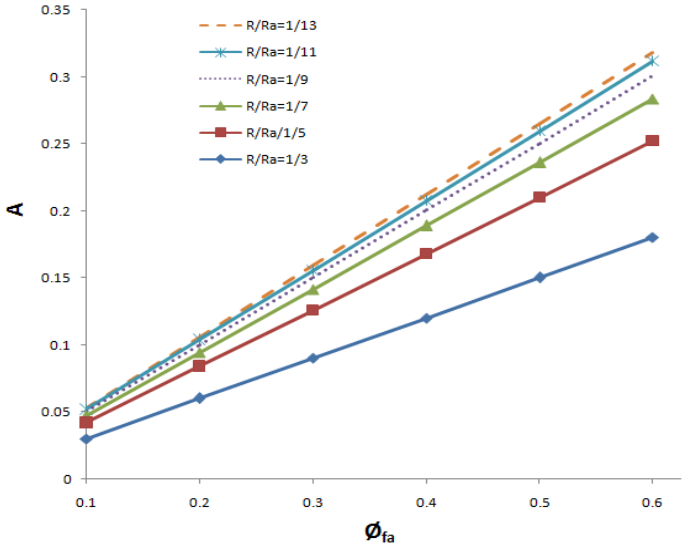
$$A = \frac{n_{fa}-n_s}{n_{fa}}(0.6\emptyset_{fa}) + \frac{n_s}{n_{fa}}(0.3\emptyset_{fa}) \quad (8)$$

The ratio of n_s/n_{fa} is dependent on the ratio of agglomerate to particle radius; $n_s/n_{fa} \approx 3R/R_a$. So, we can write;

$$A = [0.6 - 0.9\left({}^{R}/_{R_a}\right)](\emptyset_{fa}) \quad (9)$$

Finally, the effective dielectric constant of nanocomposite can be obtained by replacing the obtained expression for the A parameter into equation 7. From the above equation we can see that the A parameter increases with growth of agglomerates radius (R_a) and filler volume fraction inside the agglomerates ($\emptyset_{fa}$). It should be noted that there are limitations for $\emptyset_{fa}$ and R/R_a; $\emptyset_f < \emptyset_{fa} < 0.64$ and $R/R_a < 1/3$. At percolation the agglomerates come into each other's proximity and so even the border particles are in the neighborhood of particles from surrounding agglomerates and so the A parameter increases to $0.6\emptyset_{fa}$.

Changes in the A parameter value as a function of $\emptyset_{fa}$ and R/R_a is presented in Fig. 4. It appears that at the same agglomerate packing density ($\emptyset_{fa}$), the growth of A parameter becomes insignificant with further increase in agglomerate radius. The impact of agglomerate radius on the A parameter is more pronounced at higher agglomerate packing densities.



3. Experimental

Now, to check the validity of the proposed model in considering the effect of various filler dispersion states, several ZnO/PS samples are produced with controlled dispersion states.

3.1. Materials and equipments:

ZnO macro-particles were purchased from Nutrino Chemical Co. with average size of about 100μm. Polystyrene 336 with 20000 molecular weight was purchased from En Chun Company. Toluene with 99% purity was used as solvent and Ethanol with 96% purity was used as anti-solvent. A joint sonic (with 1.5 kW power) and shear mixing (with 12000 turns/min) device was used in order to provide suitable distribution and dispersion of particles. Dielectric measurement was carried out using a precision LCR Meter (GWINSTEK LCR-8101G) from 10^3 to 10^6 Hz.

3.2. Sample preparation

First polystyrene granules were solved in toluene and then ZnO powder was added to the mixture. Sonication along with shear mixing was used for 30 minutes in order to provide a uniform distribution of ZnO macro particles into the polystyrene matrix in a wide range of filler volume fractions (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 vol. fraction.). To separate the composite material from the solvent, ethanol was used as anti-solvent. The mixture was then left to dry for 24 hours in an oven.

To evaluate the effect of agglomerate packing density on effective dielectric constant, two composites with controlled agglomeration were produced. Both composites had the same filler volume fraction and similar sized agglomerates but different filler packing densities. To create same size agglomerates with different particle packing densities, composites containing 0.4 and 0.6 vol. fraction were grinded and passed through sieves with mesh numbers 20 and 25 to achieve composite particles with size 710 to 850 μm. These composite particles resemble same sized agglomerates with packing densities ($\emptyset_{fa}$) of 0.4 and 0.6 vol. fraction, respectively. Then the resultant composite particles were mixed with polystyrene in appropriate amounts and hot pressed to form composites with 0.3 ZnO vol. fraction. It should be noted that in the prepared composites with agglomerated microstructure, $R_a >> R$.

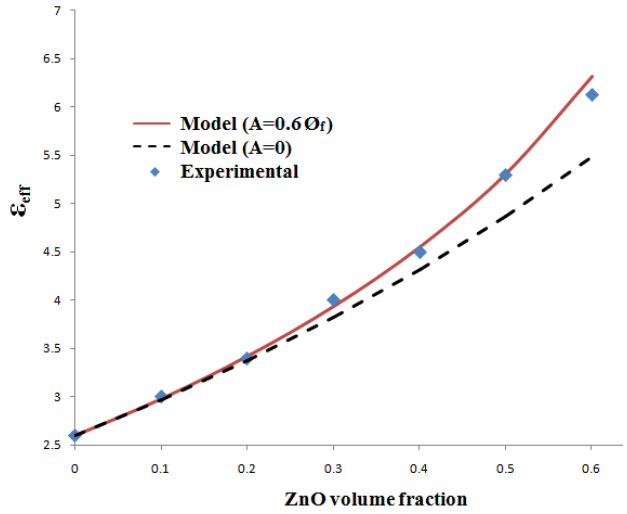
3.3. Characterization

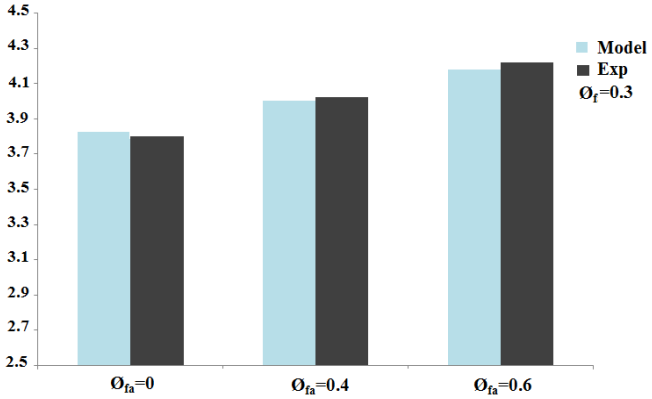
Dielectric properties measurement was performed in a frequency sweep by an LCR-meter from GW Instek, and dielectric constants of the samples were calculated using the measured capacitance.

4. Results and Discussion

Fig. 5 compares the results of the calculated and experimental dielectric constant at 10^4 Hz for ZnO/PS composites. The theoretical effective dielectric constant was calculated using equation 7 by assuming random dispersion of various volume fractions of ZnO particles with ε_f=8.9 into polystyrene matrix with ε_m=2.5; i.e. A=0.6ϕ_f. There is an excellent consistency between the experimental and the calculated effective dielectric constant which confirms the random dispersion of ZnO particles in the PS matrix. When the A parameter is dropped then the interaction between particles are not accounted for and the Maxwell-Garnett formula is retrieved. This is why there is a deviation from the predictions of the model when A=0 with the experimental data, especially at higher filler volume fractions.

The impact of agglomerate packing density on the effective dielectric constant, experimentally and theoretically, for three ZnO/PS samples with ϕ_f=0.3, and ϕ_{fa}=0, 0.4 and 0.6, is demonstrated in Fig. 6. It should be noted that since R_a>>R, then A≈0.6ϕ_{fa}. It can be seen that the effective dielectric constant increases with increase in packing density of agglomerates which can be ascribed to increased inter-particle interaction. There is a very good agreement between the results of the presented model and the experimental data.





It is realized that the developed model is successful in predicting the effective dielectric constant of composite materials with both random dispersion and agglomeration of dielectric particles. Hence, the achieved effective dielectric constant can be used for the evaluation of dispersion state of composite materials. Further experiments have been conducted in order to fully understand the impact of dispersion state on the effective dielectric constant and the ability of the developed model for characterization of dispersion which will be published hopefully in the near future.

5. Conclusion

Effect of inter-particle interaction on the effective dielectric constant was calculated as a function of filler volume fraction, volume fraction of particles inside agglomerates and agglomerate size which characterize the dispersion state in a composite. As a result, a relationship was developed between the effective dielectric constant and dispersion state in non-polar polymers filled with dielectric particles. It was shown that the effective dielectric constant increases with agglomeration of particles due to increased inter-particle interactions. The calculated dielectric constant was consistent with experimental data for both random dispersion and controlled agglomeration of particles. Hence, the developed effective dielectric constant can be used as a novel method to characterize the dispersion state in a composite.

Acknowledgements

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References

[1] Arthi Jayaraman, and Kenneth S. Schweizer, Effective Interactions, Structure, and Phase Behavior of Lightly Tethered Nanoparticles in Polymer Melts, Macromolecules, 41 (2008) 9430-9438.

[2] Otsuki, G. Bryant, Characterization of the interactions within fine particle mixtures in highly concentrated suspensions for advanced particle processing, Advances in Colloid and Interface Science, 226 (2015) 37–43.

[3] J. Liu, Y. Gao, D. Cao, L. Zhang, Z. Guo, Nanoparticle Dispersion and Aggregation in Polymer Nanocomposites: Insights from Molecular Dynamics Simulation, Langmuir, 27 (2011) 7926–7933.

[4] T. Glaskova, M. Zarrelli, A. Borisova, K. Timchenko, A. Aniskevich, M. Giordano, Method of quantitative analysis of filler dispersion in composite systems with spherical inclusions, Composites Science and Technology 71 (2011) 1543–1549.

[5] B. M. Tyson, R. K. A. Al-Rub, A. Yazdanbakhsh, Z. Grasley, A quantitative method for analyzing the dispersion and agglomeration of nano-particles in composite materials, Composites: Part B 42 (2011) 1395–1403.

[6] N. Saheb, N. Ul Qadir, M. U. Siddiqui, A. F. M. Arif, S. S. Akhtar, N. Al-Aqeeli, Characterization of Nanoreinforcement Dispersion in Inorganic Nanocomposites: A Review, Materials, 7 (2014) 4148-4181.

[7] T. V. Kosmidou, A. S. Vatalis, C. G. Delides, E. Logakis, P. Pissis, G. C. Papanicolaou, Structural, mechanical and electrical characterization of epoxy-amine/carbon black nanocomposites, eXPRESS Polymer Letters, 2 (2008) 364–372.

[8] Xingyi Huang, Liyuan Xie, Pingkai Jiang, Genlin Wang, Yi Yin, Morphology studies and ac electrical property of low density polyethylene/octavinyl polyhedral oligomeric silsesquioxane composite dielectrics, European Polymer Journal, 45 (2009) 2172–2183.

[9] S. Pegel, P. Potschke, G. Petzold, I. Alig, S. M. Dudkin, D. Lellinger, Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts, Polymer 49 (2008) 974-984.

[10] C. Calebrese, L. Hui, L. S. Schadler, J. K. Nelson, A Review on the Importance of Nanocomposite Processing to Enhance Electrical Insulation, IEEE Transactions on Dielectrics and Electrical Insulation, 18 (2011) 938-945.

[11] M. Kurimoto, H. Okubo, K. Kato, N. Hayakawa, Nanocomposite Influenced by Control of Micrometric Agglomerates, IEEE Transactions on Dielectrics and Electrical Insulation 17 (2010)662–670.

[12] B. Lively, J. Bizga, B. Li, M.G. Smith, W.-H. Zhong, Quantified non-destructive dispersion assessment via macrodispersion and AC/DC ratio analyses for hybridolycarbonate/graphite nanoplatelet/carbon nanotube composites, Composites: Part B 56 (2014) 567–574.

[13] C. Pan, K. Kou1, G. Wu1, Y. Zhang, Y. Wang, Fabrication and characterization of AlN/PTFE composites with low dielectric constant and high thermal stability for electronic packaging J Mater Sci: Mater Electron 27 (2016) 286–292.

[14] E. Allahyarov, H. Lowena, L. Zhu, Dipole correlation effects on the local field and the effective dielectric constant in composite dielectrics containing high-k inclusions, Phys.Chem.Chem.Phys., 2016, 18, 19103.

[15] M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, C.W. Reed, R. Keefe and W. Zenger, Polymer Nanocomposite Dielectrics – The Role of the Interface, IEEE Dielectrics and Electrical Insulation Society, 12 (2005) 629 - 643.

[16] R. C. Picu and M. S. Ozmusul, Structure of linear polymeric chains confined between impenetrable spherical walls, J. Chem. Phys, 118 (2003) 11239s.

[17] K. Sonoda, M. Teirikangas, J. Juuti, Y. Moriya, H. Jantunen, Effect of surface modification on dielectric and magnetic properties of metal powder/polymer nanocomposites, Journal of Magnetism and Magnetic Materials 323 (2011) 2281–2286.

[18] D. Tan, Y. Cao, E. Tuncer, P. Irwin, Nanofiller Dispersion in Polymer Dielectrics, Materials Sciences and Applications, 4 (2013) 6-15.

[19] M. Kurimoto, H. Okubo, K. Kato, N. Hayakawa, Nanocomposite Influenced by Control of Micrometric Agglomerates, IEEE Transactions on Dielectrics and Electrical Insulation, 17 (2010) 662–670.

[20] Lagendijk A, Nienhuis B, Tiggelen B. A, Vries P. Microscopic Approach to the Lorentz Cavity in Dielectrics. Physical Review Letters, 79 (1997) 657-660.

[21] Vallee R. A. L, Auweraer M. V. D, De Schryver F. C, Beljonne D, Orrit M. A Microscopic Model for the Fluctuations of Local Field and Spontaneous Emission of Single Molecules in Disordered Media. Chem. Phys. Chem., 6 (2005) 81-91.

[22] Keller O. Local fields in the electrodynamics of mesoscopic media. Physical Reports, 268 (1996) 85-262.

[23] A. Jimeno, G. Kortaberria, P. Arruti, A. Tercjak, M. Blanco, I. Mondragon, Biopolymers and Nanocomposites as Studied by Dielectric Spectroscopy, Chapter: Dynamics and

dielectric properties of polymer/nanoparticle nanocomposites by dielectric spectroscopy, Publisher: Transworld Research Network, Trivandrum, India, 2009, 31-67,.

[24] Doyle W. T, Jacobs I. S. Effective cluster model of dielectric enhancement in metal-insulator composites. Physical Review B, 42 (1990) 9319-9328.

[25] Jayasundere N, Smith B. V. Dielectric Constant for Binary Piezoelectric 0-3 Composites, Journal of Applied Physics; 73 (1993) 2462 – 2466,.

[26] Yin H. M, Sun L. Z. Magnetic properties of randomly dispersed magnetic particulate composites: A theoretical study. Physical Review B, 72 (2005) 1-6.

[27] X. Jing, W. Zhao, L. Lan, The effect of particle size on electric conducting percolation threshold in polymer/conducting particle composites, Journal of materials science letters, 19 (2000) 377 – 379.

APPENDIX A

The program for the calculation of the A parameter for $ø_f$=0.3 where there are 5 particles in the vicinity of the probe particle inside the Lorentz cavity with a radius equal to R_c=3.4R is:

```
An=0;
for n=1:1000
sumA=0;
for i=1:5
xi=2*pi*randi([0,100])/100;
ai=cos(xi);
yi=pi*randi([0,100])/100;
bi=sin(yi);
ri^3=randi([8,14]);
Ai=(3*ai*ai*bi*bi -1)/ri^3;
sumA=sumA+Ai;
end
An=sumA+An;
end
A=An/1000
```

Figures Captions:

Fig. 1. Various possible dispersion scenarios from a) random dispersion to b, c, d and e) agglomeration of particles

Fig.2 Schematic representation of Lorentz cavity and the components of the local field

Fig. 3 Treatment of agglomerates as spherical particles with a new dielectric constant

Fig. 4. Changes in the A parameter with $ø_{fa}$ and R/R_a

Fig. 5 Comparison between experimental with the calculated effective dielectric constant for random dispersion of ZnO particles in polystyrene

Fig. 6 effect of dispersion on effective dielectric properties ZnO/PS composites with $ø_f$=0.3 and $ø_{fa}$=0, $ø_{fa}$=0.4 and $ø_{fa}$=0.6

Tables captions:

Table 1. Values of A parameter for different filler volume fractions